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Chloride Mass Balances, Chloride Concentration Monitoring and Chloride Export Modelling

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1. Introduction

1.1. Context and Background Information

In seasonally frozen environments such as Canada, de-icers (chloride salts) are widely used to maintain safe driving conditions. In Ontario, the average mass of road salt (sodium chloride; NaCl) applied annually to highways and municipal roads between 2005 and 2012 that is voluntarily reported to Environment Canada is approximately 305,000 tonnes (t). It is estimated that 97% of the chloride (Cl⁻) entering rivers and lakes is derived from road salts¹. While the beneficial role of road salts for public safety is unequivocal, there are environmental consequences of their use that pose risks to stream and lake ecosystems. In the Lake Simcoe watershed, Cl is listed as a pollutant of concern in the 2009 Lake Simcoe Protection Plan², and in-stream Cl concentrations have been increasing in most tributaries since 1993³. In urbanized catchments in southern Ontario, stream Cl concentrations often exceed environmental protection guidelines set out by the Canadian Council of Ministers of the Environment (chronic: 120 mgL⁻¹; acute: 640 mgL⁻¹)⁴ during winter high flows and summer baseflow^{3,5,6}.

In urban and urbanizing watersheds, it is typical to see a trend of increasing stream CI concentrations in the winter and spring melt period⁷. These elevated CI concentrations result when winter and spring melt events transport CI in runoff from impervious surfaces to streams. Given the conservative nature of CI, it is commonly thought that CI is quickly washed off urban surfaces into the stream and that spikes in CI concentration are short-lived during the winter and spring. However, recent studies have reported elevated CI concentrations in streams that persist into the summer and, in some cases, autumn months^{8,9}. The persistence of elevated CI concentrations into the growing season presents a serious problem for aquatic biota that are sensitive to the toxic effects of CI^{10,11}. In addition, elevated CI concentrations into the summer and autumn suggest that CI transport is being delayed and/or stored along the flow path from road to stream.

The overall goal of our entire project is to improve our understanding of the relationships between the application of road salt, in-stream Cl concentrations, and stresses to stream ecosystems. This report summarizes some of our results related to the non-biological aspects of our project.

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1.2. Watershed-Scale Chloride Retention

Previous studies have suggested that CI may be stored or delayed in multiple watershed compartments on its way to the stream^{5,6,12,13}. Snow storage piles, roadside ditches with varying degrees of hydrologic connectivity to the stream network, the unsaturated zone, shallow unconfined aquifers or movement into deeper confined aquifers, the hyporheic zone, and storage within the urban karst. The annual rate of CI retention is most reliably estimated using a mass balance approach, where the amount of CI stored or retained in the watershed over one year is calculated as the difference between the mass of CI leaving the watershed in stream water and the mass of CI applied to the watershed (mainly onto impervious surfaces, such as roads and parking lots). Previous studies^{14–17} have reported net retention of CI for individual watersheds on an annual basis ranging from 28-77% using this type of approach; however, no previous studies have estimated watershed-scale CI retention for multiple watersheds for the same time period for the purpose of identifying watershed characteristics that drive inter-watershed differences in CI retention.

<u>The goal of this sub-study is to estimate and explain differences in annual, watershed-</u> <u>scale chloride storage for multiple southern Ontario watersheds that span a range of</u> <u>urbanization.</u> Our specific research objectives are to: (i) determine if the duration of elevated summer and autumn CI concentrations is increasing over time, (ii) estimate annual CI storage using a mass balance approach, and (iii) examine the relationship between CI storage and potential landscape-related drivers of CI transport from surface application to stream.

1.3. Chloride Transport from Surface Applications to Stream

Chloride travels from impervious surfaces to the stream along different flow pathways (Figure 1) and the transit time of water along those paths is important for understanding CI temporal dynamics in the stream. Where impervious surfaces are hydraulically connected to the stream we expect to see a short lag time between the wash off of road salt (due to rain, rain on snow, or snowmelt events) and peak CI concentration in the stream. However, in areas of the watershed where impervious surfaces drain into ditches and surplus water percolates to groundwater, we expect to see a longer lag time between wash off events and the CI concentration response in the stream. The goal of this sub-study is to assess the spatial variability and drivers of lags in the lateral transport of CI from surface applications to the stream. Our specific research objectives are to: (i) determine the extent to which CI concentration dynamics in different hydrological compartments are synchronous and (ii) examine whether or not a similar set of landscape variables explain the spatial variability in CI concentration response lag times between hydrological compartments across multiple watersheds. We are particularly interested in understanding how variable the CI responses in shallow groundwater, the stream hyporheic zone and the stream are, though we also invoke

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transient storage in roadside ditches and stormwater management ponds in our analyses.



Figure 1. Conceptual figure of the landscape and hydrological compartments important for the transport of chloride from surface application to streams.

1.4. Modelling Chloride Dynamics

1.4.1. INCA-CI Model of the East Holland River

The Integrated Catchment Model (INCA) was first developed for use with Nitrogen (Whitehead et al. 1988). Since then, INCA has been used to model a variety of hydrological and nutrient related factors such as nitrogen (Langusch and Matzner, 2002)(Whitehead et al. 1998), phosphorus (Wade et al. 2002) and carbon (Futter et al. 2007) with the purpose of determining impacts on water quality from land use changes and other sources (Jin et al. 2011). The model attempts to track temporal variations in hydrological flows, transformations and stores across both the land and stream portions of the catchment using reaction kinetic equations. The INCA Chloride (INCA-CI) module was first developed as a means to provide estimates of CI concentrations based on multiple input sources. The purpose was to develop a simple model that could be easily transferable to similar watersheds and which could address questions about how future CI concentrations would reflect changes in road salt regimes, including increases in the use of salt due to urbanization.

The INCA-CI model is composed of three elements, a GIS interface which is used to define catchment boundaries and to calculate the area of previously determined land use classes (to a maximum of six), a hydrological model which calculates the flow of

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rainfall as runoff, through soil water, and through groundwater stores, and a Cl input model which calculates total CI inputs to each catchment. The model functions as a lumped parameter model within each sub-catchment - however the impacts of land use and topography on flow are simulated through a semi-distributed approach. The hydrological and input models are comprised of two components, a catchment model which represents the path by which rainfall may enter the soil zone and become soil flow, direct runoff or groundwater flow. The multi-reach river model uses flows from each previous sub-catchment to maintain a mass balance along the river. Two reservoirs are used to model hydrology within each catchment - the soil zone and the groundwater zone. Data on flow rate and residence time within each zone is necessary for accurate calibration of the model, as CI can enter the stream system through either zone. The watershed is represented by subcatchments, and the stream is divided into reaches. Each reach is assigned a corresponding subcatchment and each subcatchment is user defined by a number of landscape units. The model is flexible in that values across each landscape unit are user-defined, and each "landscape unit" functions in much the same way as a hydrological response unit (HRU). The user defines all values related to soil within the landscape unit, as well as which landscape units are applicable to which subcatchments and therefore which reaches. The model produces daily simulation of flow and CI concentration of each predetermined reach in the watershed which will be compared to measured observations in order to determine model performance.

<u>The goal of this sub-study is to build a INCA-CI model of the East Holland River</u> watershed that can be used to predict the impact of future build out scenarios on CI <u>export from the watershed</u>. The East Holland River was chosen as our modelling focus because it is one of the most urbanized areas of the Lake Simcoe Region, with both Newmarket and Aurora within the boundaries. Continued urbanization is expected in this watershed over the next 20-25 years¹⁸. Our specific research objectives are to: (i) parameterize, calibrate, and verify an INCA-CI model for the East Holland River watershed, (ii) test the sensitivity of the model to a delay factor used to represent shortterm biogeochemical retention of CI in shallow organic soils, and (iii) apply different future build out and winter road maintenance scenarios in the model to evaluate impacts to CI export from the watershed.

1.4.2. Spatial Stream Network Model of the East Holland River and Willow Creek

Historically, road salt studies within watersheds have used simple mass balance or terrestrial geospatial methods that fail to capture the impacts that stream structure and directionality have on road salt fate and transport. A Spatial Stream Network (SSN) Model that accounts for data variabilities related to stream network topology and stream flow between sample sites can address these uncertainties. The goal of this sub-study is to evaluate the spatial variability in the landscape drivers of in-stream Cl concentrations among three watersheds that span a gradient of urbanization. Our specific research objectives are to: (i) collect high spatial resolution electrical conductivity data during different season for the Willow Creek, East Holland River and Mimico Creek watersheds, (ii) build separate SSN models for each watershed for each

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season, and (iii) compare the dominant landscape variables that drive in-stream Cl concentrations among the different models.

2. Methodology

We used a multi-faceted research approach to address the hydro-chemical related research questions for this project (Table 1).

Table 1. Summary of the hydro-chemical related research questions and research approaches undertaken in this project.

Specific Research Questions	Targeted Field Monitoring	Hydro- Chemical Modelling	Mining Historical Data
What is the size of the Cl storage pool			
which feeds summer baseflow CI concentrations? Has is been changing over time?			\checkmark
What is the lag time between application of			
road salt and rising in-stream Cl	\checkmark		
Does the spatial distribution of impervious areas (roads, parking lots) in a watershed	<u>/</u>		
impact in-stream CI concentration patterns and/or overall watershed retention?	·		·
As areas around Barrie and Newmarket			
urbanize, by how much are in-stream Cl concentrations likely to rise?		\checkmark	

2.1. Watershed-Scale Chloride Mass Balance Analysis

2.1.2. Study Watersheds

Twelve watersheds located within the Greater Golden Horseshoe region of southern Ontario were selected for this study (Figure 2). Selection of watersheds was based on the availability of road salt application data and continuous chloride concentration and streamflow data. Special attention was paid to selecting watersheds that spanned a gradient of urbanization from dominantly agricultural (e.g. West Holland River), to urbanizing (e.g. East Holland River), to heavily urbanized (e.g. Don River) (Table 2). The study watersheds are grouped into three different sub-regions: (i) sub-watersheds of Lake Simcoe, (ii) sub-watersheds of Lake Ontario located within the Greater Toronto Area (GTA), and (iii) sub-watersheds of Hamilton Harbour. Meteorological conditions

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vary across these sub-regions with generally colder air temperatures around Lake Simcoe and warmer air temperatures around the GTA and Hamilton Harbour.

Table 2. Watershed area and areal proportion of urban and agricultural land cover for the twelve watersheds examined as part of the CI mass balance analysis.

Watershed	Area (km²)	Urban Area (%)	Agric. Area (%)
L. Simcoe - Beaver River	329.5	4.5	35.4
L. Simcoe - Black River	319.0	6.1	24.4
L. Simcoe - East Holland River	174.7	40.3	16.4
L. Simcoe - Hawkestone Creek	40.5	6.7	24.0
L. Simcoe - Lovers Creek	59.4	27.6	29.0
L. Simcoe - Pefferlaw Brook	406.0	7.1	28.4
L. Simcoe - West Holland River	44.3	6.1	35.6
Hamilton Harbour - Grindstone Creek	81.2	14.5	25.2
Hamilton Harbour - Redhill Creek	50.6	65.0	9.7
L. Ontario - Black Creek (Humber River)	63.9	86.6	1.2
L. Ontario - Don River	314.6	80.3	2.3
L. Ontario - Etobicoke Creek	216.4	61.6	16.8

Most of the 12 study watersheds are crossed by 400 series highways (8-12 lanes wide) and/or arterial roads (2-4 lanes wide). These major roadways, as well as, smaller municipal roads are regularly salted throughout the winter season by companies contracted by the Ontario Ministry of Transportation (MTO), and upper- and lower-tier municipalities.





Figure 2. Location and boundaries of twelve study watersheds for the CI mass balance analysis. Note that watershed boundaries are delineated from the pour point where the flow and water quality data were measured.

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2.1.2. Chloride Concentration Trend Analyses

Mann Kendall trend (MKT) tests were performed on Ontario Provincial Water Quality Monitoring Network (PWQMN) data from 1993-2012 for the twelve study watersheds to assess long-term CI concentration trends (Figure 3). Mann Kendall trend tests use nonparametric statistics to evaluate whether there are monotonic increasing or decreasing trends in a data time series (Libiseller and Grimvall, 2002) and have been widely used in water quality studies around the world (Oni et al. 2013; Worrall et al. 2004; Yenilmez et al. 2011). The MKT test is a particularly useful tool in this study due to its nonsensitivity to missing values and outliers, which are frequently found in the Ontario PWQMN datasets, and also its non-sensitivity to autocorrelation in water quality data series. The MKT test was initially conducted on an annual scale (estimated from daily time series for 1993-2012) for all twelve watersheds to evaluate long term changes in stream CI concentrations. The MKT test was then applied on a seasonal scale with seasons (winter: Dec-Feb; spring: Mar-May; summer: Jun-Aug; autumn: Sep-Nov) evaluated from monthly mean values. Several watersheds (e.g. Grindstone Creek and Redhill Creek) with limited long term data sets were excluded from the seasonal and annual trend analyses.



Figure 3. Ontario Provincial Water Quality Monitoring (PWQMN) chloride concentration data from 1993-2012 for six of the Lake Simcoe sub-watersheds. PWQMN chloride concentrations are shown as annual averages.

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2.1.3. Watershed-Scale Chloride Inputs

Road salt (sodium chloride; NaCl) is the dominant source of Cl⁻ entering all 12 watersheds. In this study, other sources of Cl⁻ (e.g. precipitation, leakage of sanitary sewers, fertilizers) are assumed to be insignificant and are not quantified.

A geospatial protocol was developed to distil a large quantity of MTO and municipal road salt application data to the watershed scale. First, the shapefiles for the subwatersheds of concern and the various levels of jurisdictions to be used (municipalities, regions, patrol areas and patrol yards) were either derived from Land Information Ontario (LIO) or were acquired through personal communication with the municipality of interest. As regions (upper-level municipalities) and cities/towns/townships (lower-level) overlap geographically in Ontario, they were processed separately in order to obtain results for their roads in question. There are also unitary municipalities in Ontario (such as Toronto and Hamilton), which were clustered with the lower-level grouping for expediency. The patrol areas and yards are provincial jurisdiction and impact only provincial roads. For each of these three levels (provincial, regional and municipal), a determination of what areas geospatially intersect was carried out to determine specifically what jurisdictions for each are impacted; jurisdictional shapefiles were created for each level. Calculations of total areas and areas within the subwatersheds were also completed, in order to derive road densities.

Second, manipulation of the salt data provided by multiple sources was carried out. One set was provided by Environment Canada; it consisted of annual level (September to May) salt distribution numbers for all municipalities across Canada where it was divided up by the type of salt (NaCl, MgCl₂, & CaCl₂), state (solid or liquid), and type of application (straight, mixed with abrasives, or non-chloride; where salt contribution percentages were provided). An annual total was derived for each of the salts and then summed together to an annual chloride number based on the contribution of chlorine to the salt's atomic weight. The other data set was provided by the Ministry of Transportation (MTO) and consisted of individual files for each applicable patrol vard with daily distribution numbers by salt, sand, and liquid applications; an annual total was calculated by summing the salt as well as including the sand (comprised of 5% NaCl) and then converting it to a mass of chloride. For both sets of data, only the years 2007 to 2012 were used as only these years are present in both datasets. An important note is that the liquid components were excluded (in both the Environment Canada data and the MTO data) due to the complexity required to extract the correct data due to various formulations and inconsistent coding in the data; cursory investigation indicated that liquids contributed less than 0.1% of the salt in use.

Third, the geospatial road elements were extracted from the Ontario Road Network shapefile as provided by LIO along with several attribute tables that were required in order to properly segregate the shapefiles into pertinent components. First, as the MTO

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affects provincial roads, a shapefile of these roads was extracted by using the shield type attribute data and clipped to the buffered provincial jurisdictional shapefile. Then, for both the regional and municipal roads, extraction was completed using the jurisdiction data, and each was then also clipped to their appropriate buffered jurisdictional shapefile. A spatial join of the watersheds of concern was also completed. The number of lanes attribute table was joined to each of these three shapefiles; after calculating the length geometry of each polyline in the shapefile and then multiplying it by the number of lanes field, the resultant total length of lanes became the basic unit of distribution to be used for salt dissemination. A summarization by jurisdiction was completed for each jurisdictional shapefile so that there is a total of "lane-lengths" for the jurisdiction as well as the percentage that exists within the watershed in question.

Lastly are the rate calculations; these were completed to validate and compare various jurisdictions as well to extrapolate any gaps. Consolidating the chloride numbers from step 2 and the lane-length numbers from step 3 together into one spreadsheet allowed physically adjacent same-level municipalities to be easily compared. A review of the table showed there were many gaps and errors in the data; an effort was then made to contact all the relevant municipalities via e-mail or online submission form. While several did respond (and these numbers needed to be converted to a chloride quantity), many did not, which required filling the omissions from the adjacent municipalities. The combination of these inferred rates and the previously-provided data was used to derive the total chloride quantities that impacts each watershed based on the summation of each component jurisdiction's total chloride calculation modified by the percentage contribution of that agency's lane-lengths to the total for the watershed.

Road salt application rates by private sector contractors onto commercial, industrial, institutional and residential parking lots are not well documented despite being identified as an important source of Cl⁻ to watersheds ¹⁹. For this study, we used the relationship between lane-length density (km of lane-length per km² watershed area) and mean % parking area derived for 6 of the Lake Simcoe sub-watersheds ²⁰ to estimate the total parking area in each of the study watersheds that would receive road salt applications. We then applied the 'light' per event road salt application rate of 58.1 g m⁻² determined by Fu *et al.* (2013) and the annual number of events for each study watershed to arrive at an estimate of private sector Cl⁻ inputs.

2.1.4. Watershed-Scale Chloride Outputs

In-stream chloride loads were calculated using empirical relationships between chloride concentration and discharge. The annual cycle was divided into winter (December through April) and non winter seasons. Separate chloride - discharge relationships were specified for each season. The equation below shows the actual relationships used:

$$\ln([Cl]) = a \ln(Q) + b + \varepsilon \, during \, December - April \tag{1}$$

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$$\ln([Cl]) = c \ln(Q) + d + \delta during May - November$$
(2)

Where [CI] refers to the daily (sampled) chloride concentration, Q refers to the daily discharge, In refers to the natural logarithm, a, b, c, and d are parameters to be calibrated, and ε and δ refer to normally distributed, independent errors with a mean of zero. Note that the variance of the error distribution in the winter and non-winter terms was not assumed to be the same. Once calibrated, the parameters allow us to estimate the log-transformed concentrations for the entire period of record. The retransformation bias was addressed through an accepted Monte-Carlo method²¹. A draw from the residual distributions was added to the daily log transformed predictions of concentration, which was multiplied by the flow. These resultant daily loading estimates were summed to each of the salting years. This Monte-Carlo approach to calculating annual CI loads was iterated 1,000 times. The best estimate of the actual loads was taken as the mean of the 1,000 Monte-Carlo iterations.

The East Holland site is outfitted with a probe that measures conductivity continuously. A regression relationship between measured chloride concentrations and conductivity was used to transform the continuous conductivity measurements into continuous chloride concentration measurements. Multiplying by flow gave estimates of loading, which were aggregated to salting years. The probe-estimated annual CI loads compared reasonably well with those estimated from the concentration discharge relationships (r^2 of 0.5, slope of 1.05, n = 4).

2.1.5. Watershed-Scale Chloride Retention

A Cl⁻ mass balance analysis was carried out for all 12 watersheds from October 2007 to September 2011, inclusive, and included four winter seasons worth of salting. For these years, the annual mass of Cl⁻ released from each watershed in streamflow was subtracted from the annual mass of Cl⁻ applied to roads and private areas. For the purposes of this study, the mass of chloride exported from the watersheds through stream sediment load was assumed to be negligible. To calculate an average retention for each watershed, the average mass of retained Cl⁻ for the 4-year period was divided by the corresponding average mass of Cl⁻ input and expressed as a percentage.

2.1.6. Watershed Characterization

The ability of multiple landscape variables to explain the variability in mean annual Cl⁻ retention among our 12 study watersheds was examined. The landscape variables included watershed area, shape factor, mean slope, length of main channel, mean channel slope, area of lakes and wetlands, annual mean air temperature, annual precipitation, land use (% urban, % agricultural, % forest/wetland), and lane-length density. We also calculated an urban topological index (UTI) for each watershed which is the ratio of the distance between the centroid of the urban land use in a watershed to its pour point to the distance between the centroid of the watershed and it's pour point. Urban topological index values greater than 1 indicate urban areas that are located

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relatively far from the watershed's pour point (e.g. in headwater regions) and UTI values less than 1 represent urban areas located relatively close to the watershed outlet.

2.2. Chloride Concentration Monitoring

2.2.1. Nested Stream-Hyporheic Zone-Shallow Groundwater Sites

Electrical conductivity and water level were monitored using Solinst Levelogger LTC Junior standalone sensors in streamwater, the hyporheic zone, and shallow groundwater at 6 sites in the Willow Creek watershed (Figure 4), 1 site in the West Holland River watershed (Figure 5) and 5 sites in the East Holland River watershed (Figure 6). Stream sensors were housed in a capped PVC tube with holes drilled through it to allow water to flow through and secured to a steel 'T' bar that was pounded 3-4 feet into the stream bed. Hyporheic zone sensors were suspended inside a 1.5 m long piezometer that was slotted over its bottom 20cm and inserted a minimum of 20cm below the stream bed into the hyporheic zone (*i.e.* 20cm slotted length of piezometer extends from 20-40cm below the stream bed). Shallow groundwater sensors were suspended inside a 1.5 m long well that was slotted over its entire length and inserted into the ground to at least a 1 m depth. All slotted sections were screened to prevent sedimentation inside the wells. Continuous electrical conductivity measurements were also taken at the inlet and outlet pipes of two stormwater management ponds and in a ditch adjacent to Hwy 400 in the Willow Creek watershed (points not shown on map). All leveloggers were programmed to record every 15 minutes and baraloggers were installed nearby to record air pressure for correction of the water level data. Manual grab samples were collected bi-weekly from February 2016 to January 2017 and were analysed for major ions and alkalinity at the University of Waterloo. Chloride concentrations measured in the manual grab samples were used to develop electrical conductivity-chloride relationships for all sites.



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Figure 4. Location of nested stream-hyporheic zone-shallow groundwater monitoring sites in the Willow Creek watershed.



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Figure 5. Location of nested stream-hyporheic zone-shallow groundwater monitoring sites in the West Holland River watershed.

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Figure 6. Location of nested stream-hyporheic zone-shallow groundwater monitoring sites in the East Holland River watershed.

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2.2.3. Cross-Correlation Analysis of Lateral and Longitudinal Chloride Dynamics

Cross-correlation analysis was used to estimate the mean time lag between the Cl response to wash-off events in shallow groundwater, the hyporheic zone and streamwater at all of the nested monitoring sites in Willow Creek and East Holland River. The same approach was also used to estimate the mean lag time in a longitudinal direction between stream and hyporheic zone sites that are flow-connected.

Final reporting upon completion of Masters of Spatial Analysis thesis by Bhaswati Mazunder (anticipated defence December 1 2017)

2.3. Modelling Chloride Dynamics

2.3.1. INCA-CI Model of the East Holland River

Development of the INCA-CI model for the East Holland River watershed involved four main steps: (i) model parameterization, (ii) derivation of model inputs, (iii) model calibration, and (iv) model verification. Land use and other spatial data (e.g. surficial geology) necessary for the parameterization of the terrestrial and geographic information system (GIS) components of the INCA-CI model were acquired from the Southern Ontario Land Information System, and the Ontario Flow Assessment Tool.

The INCA-CI model inputs include daily precipitation and temperature data, daily hydrologically effective rainfall and soil moisture deficit, and chloride inputs. For the meteorological data, data from three Environment Canada climate stations, Newmarket, Aurora, and Uxbridge were necessary to develop a complete time series for the modelled period. Chloride inputs are required on a kg/ha/day basis. Previous work on modelling the mass balance of chloride across multiple subwatersheds within the Lake Simcoe region (Giberson, 2016) will be used to determine the salting rate per lane length on a yearly basis, providing the necessary inputs to the model.

Daily hydrologically effective rainfall and soil moisture deficit were modelled using PERSiST (Precipitation, Evapotranspiration and Runoff Simulator; Futter et al. 2016). PERSiST is a semi-distributed rainfall-runoff model, which simulates flow at one or more points within a river network. It requires daily time series of temperature, and precipitation, in addition to landscape characteristics which may impact the physical processes associated with runoff. PERSiST functions in a manner similar to INCA, in which simulations for terrestrial runoff and streamflow are provided on a semidistributed, watershed scale. It makes use of the same subcatchment model, wherein the watershed is divided into subcatchments, which are divided into a series of userdefined "landscape units" which can be seen as analogous to hydrological response units. Each landscape unit functions independently as a water store with a unique hydrological response. The model functions within a hierarchical structure. The watershed is divided into smaller subcatchments, each of which has a one-to-one relationship with a stream reach. All model calculations are done sequentially beginning with the terminal (furthest upstream) reach. The model requires daily temperature and precipitation data provided by the user, in addition to data on discharge at the terminal

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point at reach for calibration purposes. PERSiST was designed to produce compatible data input files for the INCA family of models. PERSiST generates files for both subcatchment and watershed scale measures. Soil moisture deficit is calculated as the difference between the depth of water in each bucket and the bucket's maximum water holding capacity. Hydrologically effective rainfall is calculated as the difference between actual precipitation minus interception and evapotranspiration.

Multiple sources were used to provide the data on flow and chloride concentrations necessary for the validation of the model. A long term stream gauge at Holland Landing (maintained by the Lake Simcoe Conservation Authority) captures discharge and conductivity for the years 2002-2016. The Provincial Water Quality Monitoring Network (PWQMN) also maintains a monitoring station at Holland Landing, for which Chloride concentrations are available for 2002-2011. Owing to data availability, the entire subwatershed was treated as a single catchment and reach during the modelling process. As the focus of the study is to test scenarios related to the delivery of chloride to Lake Simcoe, a single point at which to model outgoing chloride concentrations is suitable.

Final reporting upon completion of Masters of Spatial Analysis thesis by Mallory Carpenter (anticipated defence August 15 2017)

2.3.2. SSN Model of Willow Creek and East Holland River

The SSN model for chloride concentrations requires high spatial resolution in-stream measurements. To build this dataset, a series of longitudinal electrical conductivity surveys were carried out in July 2016, October 2016, February 2017 and April 2017 in the East Holland River, Willow Creek and Mimico Creek watersheds (Figure 7). These watersheds represent a gradient of urban land use. The surveys took place over 2-4 days when no rainfall occurred (precipitation inputs alter the in-stream conductivity patterns) and consisted of measuring stream electrical conductivity using a YSI EXO2 water quality sonde at sites located approximately every 500 m along the stream network (Figure 3). Biweekly manual grab samples from a subset of sites where continuous electrical conductivity monitoring was being carried out were analyzed for chloride concentration and these results were used to develop electrical conductivity-chloride relationships for each watershed.

The SSN model allows us to assess the spatial auto-covariance between the sites by restricting weighted autocorrelation functions to measure across up-stream connected sites or down-stream connected sites. Restricting our analysis to either up-stream or down-stream connected sites means that any flow-unconnected sites are not compared and thus are not included in the model. Covariates are used to try and explain the relationship between in-stream conductivity and landscape variables. Some covariates include hydrological properties, such as surface water contributing area and potentially baseflow chloride concentrations. Land use properties are also included with pertinent classifications including Community/infrastructure area, lane-length per km², agricultural land, and non-developed land. We aim to include chloride application density and rates

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once relevant weather events can be quantified for the 2017 winter season. Other landscape properties to be used as covariates include geographic characteristics, such as slope and the stream length, and we will also include surficial geological classifications.

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Figure 7. Maps of the study watersheds and sample sites used for the high spatial resolution longitudinal electrical conductivity surveys.

3. Results and Discussion

3.1. Chloride Retention Across Southern Ontario Watersheds

3.1.1. Chloride Concentration Trends

Here we only report results for the sub-watersheds located within the Lake Simcoe watershed. Mann Kendal Trend tests indicated significant increasing trends in mean annual stream CI concentrations in some non-urbanized watersheds (e.g. Black River and Pefferlaw River; Figure 8). However, mean annual CI concentration in these systems is still below the chronic and acute CI toxicity levels, 210 mg L⁻¹ and 640 mg L⁻¹ , respectively. In contrast, mean annual stream CI concentrations are well above the chronic CI toxicity level in all of the highly urbanized watersheds (Figure 8). Three of the more urbanized watersheds (Lovers Creek, East Holland River, Pefferlaw Brook) showed significant increases in annual CI concentrations between 1993-2012 (Table 3). Also, large variations existed in mean annual stream CI concentrations in urbanized watersheds where we observed no significant increasing trends (Figure 8 and Table 3). While the annual trends are useful for an overview of long-term changes in stream CI concentrations, an examination of seasonal trends is required to infer differences in CI retention across the gradient of urbanizing watershed being considered here. At the seasonal scale, Black River, Pefferlaw River and Lovers Creek all showed significant monotonic increasing trends in all seasons (Table 3). All watersheds except the Beaver River and the West Holland River showed increasing CI concentration trends in the summer and autumn seasons. West Holland River only showed increases in the spring season (Table 3).

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Figure 8. Mann Kendall Trend analysis of mean annual chloride concentration for the six sub-watersheds located within the Lake Simcoe watershed.

Table 3. Seasonal trends of stream CI concentrations across a gradient of urbanizing Lake Simcoe tributary catchments. The shaded months show hot moments in stream CI concentration where the Mann-Kendall (MK) value > 4.

	Seasonal Stream CI trends										Annual		
Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	trends
Lovers	++++	++++	+++	++++	++++	++++	++++	++++	++++	++++	+++	++++	++++
East Holland		+		+++	++	++	++	+++	+++	+++	+		+++
Pefferlaw	++++	++++	++	+++	+++	++++	++++	++	++++	++++	++++	++++	++++
Black	++++		++	+++	++++	+++	++++	++++	++++	++++	++	++	++++
West Holland			+++							+++	++		+
Beaver													
Note: $p_{2}(0,0) = (1,1,1) = (0,0) = (1,1) = (0,0) = (1,1) = (0,0) = (1,1) = (0,0) = (1,1) =$													

Note: p<0.000 = ++++, p<0.01 = +++, p<0.5 = ++, p<0.1 = +

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3.1.2. Watershed-Scale Chloride Retention

Chloride inputs from winter maintenance activities were estimated using the geospatial approach (ref Giberson thesis) for all twelve watersheds for the 2007-2010 period (Figure 9).



Figure 9. Maps of average annual chloride application rates onto roadways in the twelve study watersheds

These inputs were coupled with Cl outputs for the same time periods to estimate mean annual Cl retention (expressed as a % of inputs) for all twelve watersheds for 4 years (2007-2010). For all watersheds and all years, we estimated a net storage of Cl and mean annual Cl retention ranged from 38-90%. Two watersheds, West Holland River and Etobicoke Creek, had mean annual Cl retention values well below the other 10 watersheds and upon further inspection we realized that our estimates for these two watersheds may be inaccurate. For West Holland River, there were issues with temporal and spatial overlap of the flow and Cl concentration data that may have results in a large overestimate of the outputs and for Etobicoke Creek we are concerned that we have underestimated inputs by neglecting to consider the application of de-icing agents at the Pearson International Airport whose property intersects the watershed. We have elected to leave these two watersheds in our landscape analysis for now until we can fully resolve these issues.

To better understand the processes that drive the long-term retention of Cl in watersheds, we looked at the relationship between mean annual Cl retention and mean annual Cl inputs (Figure 10), watershed lane-length density (Figure 11), and the spatial distribution of urban land cover in the watershed (Figure 12).



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Figure 10. Relationship between watershed-scale mean annual chloride retention and mean annual chloride inputs.







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Figure 12. Relationship between watershed-scale mean annual chloride retention and the spatial distribution of urban land use (note that values >1 represent urban land use that is relative far from the outlet of the watershed).

Interestingly, we found a negative relationship between mean annual CI retention and CI inputs and watershed lane-length density. Although not intuitive, we believe this relationship stems from the fact that more urbanized watersheds (i.e. ones with higher lane-length density and road salt inputs) are more likely to have their impervious surfaces hydraulically connected to the stream via storm sewers. These direct connections from impervious surfaces to streams minimize the infiltration of saline water into the soil and transport via percolation into groundwater, thereby decreasing overall CI retention. Although strongly driven by our two anomalous CI retention values for West Holland River and Etobicoke Creek, the positive relationship between mean annual CI retention and our newly-developed urban land use spatial distribution index suggests that CI retention increases when urban areas are located further from the watershed outlet. Presumably this can be explained by longer flow pathways carrying chloride through the watershed and hence taking a longer amount of time. We are working on refining this spatial distribution index to consider which urban areas are hydraulically connected to the stream and which drain into adjacent pervious surfaces.

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3.2. Chloride Concentration Dynamics in Different Hydrologic Compartments

Relationships between continuous electrical conductivity measurements and chloride concentrations from bi-weekly grab samples were strong (all sites had r^2 >0.75) and allowed us to calibrate our entire dataset of continuous electrical conductivity measurements to CI concentration. In-stream CI concentration data from flow connected sites in each watershed (example for East Holland River shown in Figure 13) will be analyzed using cross-correlation analysis for longitudinal lag times. Similar data exist for the hyporheic and shallow groundwater sensors in East Holland River and all hydrologic compartments in Willow Creek. Nested monitoring data from each site (example for the lower East Holland River site shown in Figure 14) will also be used to examine lags in the transport of CI between shallow groundwater, the hyporheic zone and the stream.

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Figure 13. Continuous in-stream chloride concentration measurements from nested catchment sites in the East Holland River.



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Figure 14. Continuous chloride concentration data for the lower East Holland River site including data from the stream (EH_S1), hyporheic zone (EH_H1), shallow groundwater near the stream (EH_G1) and shallow groundwater at the base of the valley slope (EH_G2).

3.3. INCA-CI Model for the East Holland River Watershed

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3.4. Spatial Stream Network Model of Chloride Concentrations in East Holland River and Willow Creek

A SSN model has been successfully developed for the East Holland River (Figure 15). This model uses basic spatial relationships between in-stream conductivity and urban land use to develop a predictive map of in-stream chloride concentrations in this watershed.

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Figure 15. Results of the SSN model for specific conductivity (a surrogate for chloride concentrations) in the East Holland River.

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4. Implications for Watershed Management and Future Research Directions

Our results will be shared with our conservation authority partners to help inform and support their efforts to develop adaptive winter maintenance management strategies for Southern Ontario. In particular, our INCA-CI and SSN model results will improve predictions of watershed CI export under future urban development scenarios and will improve in-stream chloride concentration predictions in un-sampled areas, respectively. Our strategically located, nested monitoring will allow for a better understanding of the spatial relationships between surface applications of chloride, landscape characteristics (e.g. land cover & surficial geology), and in-stream chloride concentrations. Over the longer term, our high frequency field data will be used to improve the calibration, and hence accuracy of our models.

Future research will include integration of flow direction and hydraulically connected areas into our spatial distribution of urban land use index, and the development of an INCA-CI model for the Willow Creek watershed.

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